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(54) IMPROVEMENTS IN OR RELATING TO HYDROCARBON RESINS

(71) We, NIPPON OIL COMPANY, LIMITED, a corporation organised and existing under the laws of Japan, of 3—12, Nishi Shimbashi 1-chome, Minato-ku, Tokyo, Japan, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for producing hydrocarbon resins with regulated softening point.

Solvent-soluble resins with controlled softening point are desirable for various applications, such as for use in paint, printing ink, adhesives, paper sizing and rubber compositions. It is already known according to United States Patent Specification No. 2,689,231 to polymerise thermally a mixture of cyclopentadiene, or a dimer thereof, i.e. dicyclopentadiene, and a reactive monomer containing vinyl radical in the absence of solvent and catalyst, but the resin obtainable from dicyclopentadiene and styrene according to this process is provided with a softening point as high as 199—201°C and therefore has limited applications. Also United States Patent Specification No. 3,468,837 discloses a process in which a resin having a softening point as high as 170—200°C by means of thermal polymerisation of a cracked oil fraction rich in dicyclopentadiene and with added α -pinene, but the softening point cannot be controlled to a desired value in this process. Furthermore, another known process of polymerising a mixture of cyclopentadiene or dimer thereof, i.e. dicyclopentadiene, and unsaturated aromatic hydrocarbons such as styrene in the presence of Friedel-Crafts catalyst allows control of the softening point to a certain extent, but the product in this process cannot be made inexpensive on an industrial scale since the use of such catalyst requires an additional step of removal after the polymerisation. Besides, in such polymerisation

employing Friedel-Crafts catalyst, a high content in cyclopentadiene will lead, during the polymerisation, to the formation of a gelled substance which remains suspended in the reaction product and lowers the yield. Furthermore, the resins thus obtained are generally provided with a relatively low softening point and are unstable in air to become insoluble in organic solvents after prolonged standing in air.

Thus, the resins thermally polymerised from cyclopentadienes and unsaturated aromatic hydrocarbons such as styrene have scarcely been used in practical applications because of excessively high softening point despite favourable properties thereof such as a sufficiently high stability against oxidation and a suitable degree of unsaturation in comparison with the polymers obtained by the use of Friedel-Crafts catalyst.

More specifically as to the softening point, the resin for use in paints is preferred to have a softening point ranging from 130° to 160°C. in order to be used in combination with drying oils, while the preferred temperature range of softening point is 80—100°C. and 50—60°C., respectively, in case of adhesives or rubber compositions and in paper sizing agents. Although there has been a great deal of demand in various fields for resins with controlled softening points as explained above, it has not been made possible to control nor even to lower the softening point according to the purpose in a synthesis of resin.

It is an object of the present invention to overcome or at least mitigate the above-mentioned, and other, disadvantages.

According to the present invention there is provided a process for producing a hydrocarbon resin, which process comprises thermally polymerising cyclopentadiene, methylcyclopentadiene or Diels-Alder oligomer(s) thereof with unsaturated aromatic hydrocarbon(s) at a temperature in the range of from 200° to 350°C in the presence of a controlled amount

[Price 25p]

of an inert hydrocarbon solvent capable of dissolving the aforementioned two reactants.

According to this invention, the softening point of the resins which are obtainable by thermally polymerising, in the absence of catalyst, a mixture of cyclopentadiene, methylcyclopentadiene or Diels-Alder oligomers thereof and unsaturated aromatic hydrocarbons such as styrene or an oil fraction rich in said hydrocarbons, can be easily and freely controlled by adding suitable hydrocarbon solvents into the starting materials of said polymerisation and modifying the amount of said solvents.

The first starting material employed in the process of this invention is cyclopentadiene, methylcyclopentadiene or Diels - Alder oligomers thereof (for example in case of cyclopentadiene, dicyclopentadiene, tricyclopentadiene or tetracyclopentadiene can be used as the starting material, leading to the same product).

Cyclopentadiene, methylcyclopentadiene or the oligomers thereof employed as the first starting material in the process of this invention are not necessarily required to be of high purity, and it is possible to use a concentrated fraction which is obtained by thermally dimerising a C_5 -fraction in the by-product of thermal decomposition of naphtha, thereby converting cyclopentadiene, and methylcyclopentadiene contained therein into dicyclopentadiene, dimethylcyclopentadiene, cyclopentadiene - methylcyclopentadiene codimer, cyclopentadiene - isoprene codimer, cyclopentadiene - piperilene codimer and so on and by removing the major portion of the C_5 -components such as C_5 -olefins, C_5 -paraffins and the like by distillation from said C_5 -fraction.

The second starting material to be employed in the process of this invention is unsaturated aromatic hydrocarbon(s) such as styrene, alkylated derivative(s) thereof for example α - or β -methylstyrene, *o*-, *m*- or *p*-vinyltoluene, indene or alkylated derivatives thereof, and it is also possible to use a fraction of the above-mentioned substances obtained as a by-product by the decomposition of oil containing such substances. Pyrolysed oil fractions containing unsaturated aromatics usually contain alkyl aromatic components, which can be used as the solvent component, as will be explained hereinafter.

In polymerising the mixture of the above-mentioned first and second starting materials, the total monomer content, that is the first and second starting materials together, with respect to the entire mixture is preferred to be within a range of from 10 to 95 wt. % while the remaining portion of said mixture is composed of the solvent component explained hereinafter. Also the ratio of mixing by weight of the first and second starting

materials is preferred to be within a range of 5/95 to 95/5.

The solvent component to be employed in the process of this invention is an inert hydrocarbon solvent or a mixture of inert hydrocarbon solvents, which is capable of dissolving the mixture, as used in the process, of cyclopentadiene, methylcyclopentadiene or Diels-Alder oligomers thereof and unsaturated aromatic hydrocarbon such as styrene, said solvent component being represented for example by aromatic hydrocarbons such as benzene, toluene and xylene, hexane, isooctane, mineral spirit, solvent naphtha and kerosene. The use of such solvent component enables one to control the softening point of the produced resin according to the amount of said solvent added, that is a larger amount of solvent component within the above-mentioned range leads to a lower softening point, and *vice versa*.

The reaction temperature, an extremely important factor in the process according to this invention, should be maintained within a range of from 200 to 350°C, preferably from 250 to 280°C and the resin soluble in solvents and meeting the object of the present invention is solely obtainable at a reaction temperature within the above-mentioned range. A reaction temperature lower than 200°C leads to the formation of gel and of resin partly insoluble in solvents, while a reaction temperature exceeding 350°C shows a tendency to provide a black carbon-containing substance due to the decomposition of the resin.

The reaction period is usually preferred to be within a range of from 10 min. to 20 hours, though it is dependent on the reaction temperature to some extent. A longer reaction period generally leads to a higher softening point of the produced resin, while an excessively short reaction period results in the interruption of reaction at a stage where the resultant polymer is partly insoluble and unmeltable. Consequently the reaction should preferably be continued until such insoluble substance completely disappears. The resin is generally obtained, after the reaction, by removing the solvent component and unreacted monomers by means of vacuum distillation or steam distillation from the reaction mixture.

Because of the use of a relatively high temperature in the process according to the present invention, the reaction is preferably carried out in a pressure-durable reactor provided with a pressure gauge and a thermometer, with or without agitation. Also, the process of the present invention can be realised either batchwise or continuously. Additionally, the reaction system is preferably placed in an atmosphere of inert gas such as nitrogen or carbon dioxide.

Thus by utilising the process of the present invention the softening point of the resin pro-

duced can be generally easily and freely controlled within a range of ca. 40—195°C by polymerising a mixture of cyclopentadiene, methylcyclopentadiene or Diels - Alder oligomer(s) thereof and unsaturated aromatic hydrocarbon(s) such as styrene, together with a controlled amount of an inert hydrocarbon solvent, under the defined conditions.

An increase of the amount of solvent with respect to a fixed mixing ratio of the first and second starting materials enables one to lower the softening point while the resin composition is maintained constant. Since the softening point of the resin is apparently solely determined by the ratio of solvent to the starting materials, the amount of aromatics in the resin is controllable independently of the desirable softening point, and it is thus made possible to obtain the resins most suitable for various applications.

The process of the present invention is characterised in the possibility of controlling the softening point and the aromatics content in the resin independently. For example, as shown in the following Examples, it is possible to obtain resins with a fixed CPD/aromatics ratio of ca. 7:3 but with different softening points such as 58°, 80°, 106°, 130°, 155°C, etc.

According to the process of this invention, the softening point of the resin can apparently be controlled easily in accordance with the following general formula:

$$T_m = A + B(T - 250) - C[A_r] - D[S],$$

wherein T_m represents the softening point of the resin formed (°C),

T represents the reaction temperature in the range of from 200 to 350°C (°C),

$[A_r]$ represents the concentration of the second starting material contained in the monomer (cyclopentadienes as the first starting material and unsaturated aromatics components as the second starting material) (moles/litre),

S represents the concentration of the solvent in the reaction system (moles/litre), and A , B , C and D are each constants.

Accordingly, in this invention, a resin having a definite softening point may be obtained by carrying out a preliminary experiment under some arbitrary conditions in order to find the value of the constants shown above, selecting the reaction conditions (T , $[A_r]$, $[S]$) so that the intended resin may be formed, and subsequently by conducting polymerisation reaction.

In this invention, for example, the respective value of the constants, when dicyclopentadiene is used as the first starting material, styrene as the second starting material, and commercial xylene as the solvent, is as follows:—

A ; About 180,
B ; About 1,
C ; About 10,
D ; About 14.

On the other hand, it is also possible to produce resins provided with a fixed softening point for example 90°C, but with different CPD/aromatic ratios such as 8:2, 7:3, 1:1, 3:7, 2:8 etc.

This possibility is extremely significant in consideration of the generally accepted fact that a hydrocarbon resin of this kind with a fixed composition is unable to be provided with a variable softening point.

Features which can show advantage to the present invention are summarised as follows:—

(1) the process is capable of providing resins most suitable for extremely diversified applications as the mixing ratio of the first and second starting materials can be adjusted to provide a desirable resin composition meeting the purpose intended while the softening point is independently controllable according to the purpose of use,

(2) the process enables extremely easy and free regulation of the softening point of the produced resin,

(3) the process is capable of producing almost colourless resins which are soluble in hydrocarbon solvents such as benzene, toluene, xylene, solvent naphtha, a hydrocarbon solvent which has a boiling range of 270—310°C and an Aniline point of ca. 72°C mutually soluble with drying or semi-drying oils such as linseed oil, soybean oil or safflower oil and are denatured by said drying oils by simple heating,

(4) the process is capable of producing resins provided with unsaturation corresponding to a bromine number ranging from 30 to 120, which facilitates various denaturing such as with the addition of maleic anhydride. Consequently, the resins are far more adapted, in comparison with the resins of high softening points obtainable with prior processes, for use in paints, printing inks, paper sizing agents, adhesives, rubber compositions etc.

(5) the resins obtainable with the process according to this invention generally exhibit excellent stability against oxidation, showing no change after standing in the air for more than one month and only limited oxidation even after prolonged exposure to air at 200°C. Thus, the resins are free from the deterioration by oxidation in ordinary conditions of use for example as a coating agent, etc. Ordinary antioxidants, such as 2,6 - di - tert - butyl phenol, may be added, however, to the resin if necessary in case of use under drastic conditions.

The following Examples illustrate the present invention.

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Example 1.

Dicyclopentadiene (DCPD), styrene and commercially available mixed xylene of industrial grade as the solvent were reacted for 3 hours at a temperature of 260—265°C in an autoclave provided with a stirrer. The autoclave was cooled after the reaction had been terminated, and the reaction mixture was dis-

tilled under reduced pressure to remove unreacted monomer and the solvent, thereby obtaining the resin as the reaction product. The following Table 1 shows the properties of resin obtainable when the concentration of solvent is changed from 10 to 90 wt.% while the DCPD/styrene weight ratio is kept constant at 70/30.

TABLE 1

No.	Solvent concentration (wt. %)	Properties of product			
		(*1) Softening point (°C.)	(*2) Colour	(*3) Bromine Number	Solubility in benzene
1	90	58	5	80	soluble
2	70	80	5	76	"
3	50	106	6	64	"
4	30	130	6	68	"
5	10	155	6+	66	"

(*1) Measured according to JIS—K—2531—60

(*2) Colorimetry on Gardner scale according to ASTM—D—1544—58 T; sample 2 gr. in benzene 25 cc.

(*3) Measured according to ASTM—D—1158

Foregoing Table 1 shows that the decrease of solvent (concentration) at a constant DCPD/styrene weight ratio of 70/30 results in the elevation of softening point, and thus clarifies the control of softening point by means of solvent amount, which is a principal object of this invention.

The resins shown in foregoing Table 1 were soluble in benzene, toluene, xylene, hydrocarbon solvent having a boiling range of 270—310°C and an Aniline point of ca. 72°C and solvent naphtha, and could be made into a useful coating material by cooking with linseed oil or soybean oil. In addition, the resins, for example the resin No. 4, could be transformed into a resin provided with high softening point and polar radical particularly adapted for use in paints, printing inks etc. by the addition of maleic anhydride thereto.

On the other hand, a similar reaction with similar starting materials but excluding the

solvent resulted in a resin product with a softening point exceeding 200°C, which cannot be changed even under modified reaction conditions. Also, the starting materials for resin No. 3 give rise, when reacted for 25 hours at 180°C, to an almost gel product, of which a very limited portion is soluble in benzene.

Example 2.

DCPD, mixed *o*-, *m*- and *p*-vinyltoluene and industrial-grade toluene as the solvent were polymerised thermally for 3 hours at a temperature of 270—275°C in an autoclave provided with a stirrer, and the reaction mixture was treated similarly to that of Example 1 to obtain the resin product. Following Table 2 shows the properties of the resins obtained under various solvent concentrations with a constant DCPD/vinyltoluene weight ratio of 70/30.

TABLE 2

No.	Solvent concentration (wt. %)	Properties of product			
		Softening Point (°C.)	Colour	Bromine number	Solubility in benzene
6	60	85	3	70	soluble
7	40	112	4-	70	"
8	20	135	5	68	"

Foregoing Table 2 shows that the softening point was controllable by the amount of solvent also in case of toluene. The resins Nos. 6 to 8 were soluble in benzene, toluene, xylene, hydrocarbon solvent having a boiling range of 270—310°C and an Aniline point of ca. 72°C and solvent naphtha, and also mutually soluble with linseed oil or soybean oil and could be made, by cooking therewith, into a coating material. Furthermore, said resins were mutually soluble with phenol resins in any arbitrary ratio.

Example 3.

DCPD and a C₆-fraction with a boiling range of 140—200°C obtained from a pyrolysed oil by-product from the steam cracking of naphtha were thermally polymerised for 3 hours at a temperature of 260—265°C in an autoclave provided with a stirrer, and the reaction mixture was treated similarly to that in Example 1 to obtain the resin product. Following Table 3 shows the properties of resins obtained with various ratios by weight of DCPD/C₆-fraction.

TABLE 3

No.	DCPD concentration (wt. %)	Properties of product			
		Softening point (°C.)	Colour	Bromine number	Solubility in benzene
9	10	75	7	75	soluble
10	30	103	6+	75	"
11	50	127	6	73	"
12	70	156	5	73	"
13	80	170	5	72	"

From foregoing Table 3, it is clear that the softening point of the resulting resin was controlled by changing the amount of C₆-fraction containing solvent components. The obtained resins Nos. 9—13 were soluble in benzene, toluene, xylene, hydrocarbon solvent having a boiling range of 270—310°C and an Aniline point of ca. 72°C and solvent naphtha, and mutually soluble with linseed oil or soybean oil to form a coating agent by cooking therewith.

Example 4.

A first starting material consisting of a high-boiling residue (containing 88 wt.% of

dicyclopentadiene 1.2 wt.% of methylcyclopentadiene dimer, 9.5 wt.% cyclopentadiene codimer with isoprene or piperylene and 2.3 wt.% C₆-fraction) obtained by heating a C₆-fraction of pyrolysed oil produced by steam cracking of naphtha for 4 hours at 100°C followed by removal of the C₆-fraction by distillation, and a second starting material consisting of styrene and commercially available xylene of industrial grade were reacted for 3 hours at a temperature of 270—275°C in an autoclave, and then the reaction mixture was treated similarly to that in Example 1 to obtain the resin product.

Following Table 4 shows the properties of the first starting material/styrene of 50/50 resins obtained under a fixed ratio by weight and with variable solvent concentrations.

TABLE 4

No.	Solvent concentration (wt. %)	Properties of product			
		Softening point (°C.)	Colour	Bromine number	Solubility in benzene
14	50	85	4	65	soluble
15	30	109	4	68	"
16	10	135	4	65	"

The resins Nos. 14 to 16 of Table 4 were soluble in benzene, toluene, xylene, hydrocarbon solvent having a boiling range of 270—310°C and an Aniline point of ca. 72°C and solvent naphtha. In a polymerisation employing Friedel-Crafts catalyst with an elevated content of cyclopentadiene as indicated above, it was impossible to obtain resins which were pale-coloured and soluble in benzene as shown in Table 4. Thus, the process according to the present invention provides the advantage of enabling control of the softening point easily even in a case of using a reactive material such as cyclopentadiene.

Example 5.

Methylcyclopentadiene, styrene and solvent naphtha as the solvent component were subjected to thermal polymerisation for 3 hours at a temperature of 265—270°C in an autoclave provided with a stirrer, and then the reaction mixture was processed similarly to that in Example 1 to obtain the resin product. Following Table 5 shows the properties of the resins obtained under a fixed methylcyclopentadiene/styrene ratio by weight of 70/30 and with various solvent concentrations.

TABLE 5

No.	Solvent concentration (wt. %)	Properties of product			
		softening point (°C.)	Colour	Bromine number	Solubility in benzene
17	50	110	5	72	soluble
18	30	124	5+	70	"
19	10	145	5	68	"

The resins Nos. 17 to 19 were soluble in benzene, toluene, xylene, hydrocarbon solvent having a boiling range of 270—310°C and an Aniline point of ca. 72°C and solvent naphtha.

Example 6.

Cyclopentadiene, styrene and isooctane were reacted for 2 hours at a temperature of 270—

280°C in an autoclave, and then the reaction mixture was processed similarly to that in Example 1 to obtain the resin product.

Following Table 6 shows the properties of the resins obtained under a fixed cyclopentadiene/styrene ratio by weight of 50/50 and with solvent concentrations modified within the range of 20 to 60 wt.%.

TABLE 6

No.	Solvent concentration (wt. %)	Properties of product			
		Softening Point (°C.)	Colour	Bromine number	Solubility in benzene
20	60	86	4	67	soluble
21	40	100	4	65	"
22	20	125	3	65	"

The resins No. 20 to 22 were soluble in benzene, toluene, xylene, hydrocarbon solvent having a boiling range of 270—310°C and an Aniline point of ca. 72°C and solvent naphtha, and mutually soluble with linseed oil or safflower oil to form a coating agent after cooking therewith.

WHAT WE CLAIM IS:—

1. A process for producing a hydrocarbon resin, which process comprises thermally polymerising cyclopentadiene, methylcyclopentadiene or Diels-Alder oligomer(s) thereof with unsaturated aromatic hydrocarbon(s) at a temperature in the range of from 200° to 350°C in the presence of a controlled amount of an inert hydrocarbon solvent capable of dissolving the aforementioned two reactants.
2. A process according to Claim 1, wherein the unsaturated aromatic hydrocarbon is styrene, a methyl styrene and/or a vinyl toluene.
3. A process according to Claim 1 or 2, wherein the monomer concentration is in the range from 10 to 95 wt. %.
4. A process according to Claim 1, 2 or 3, wherein from 5 to 95 parts by weight of unsaturated aromatic hydrocarbon(s) is used per 100 parts by weight of monomers.
5. A process according to any one of the preceding claims, wherein the inert hydrocarbon solvent is benzene, toluene, xylene, hexane, isooctane, mineral spirit, solvent naphtha or a mixture of any thereof.
6. A process for producing a hydrocarbon resin, substantially as described in foregoing Example 1 in connection with Resin 1.
7. A process for producing a hydrocarbon resin, substantially as described in foregoing Example 1 in connection with Resin 2.
8. A process for producing a hydrocarbon resin, substantially as described in foregoing Example 1 in connection with Resin 3.
9. A process for producing a hydrocarbon resin, substantially as described in foregoing Example 1 in connection with Resin 4.
10. A process for producing a hydrocarbon resin, substantially as described in foregoing Example 1 in connection with Resin 5.
11. A process for producing a hydrocarbon resin, substantially as described in foregoing Example 2 in connection with Resin 6.
12. A process for producing a hydrocarbon resin, substantially as described in foregoing Example 2 in connection with Resin 7.
13. A process for producing a hydrocarbon resin, substantially as described in foregoing Example 2 in connection with Resin 8.
14. A process for producing a hydrocarbon resin, substantially as described in foregoing Example 3 in connection with Resin 9.
15. A process for producing a hydrocarbon resin, substantially as described in foregoing Example 3 in connection with Resin 10.
16. A process for producing a hydrocarbon resin, substantially as described in foregoing Example 3 in connection with Resin 11.
17. A process for producing a hydrocarbon resin, substantially as described in foregoing Example 3 in connection with Resin 12.
18. A process for producing a hydrocarbon resin, substantially as described in foregoing Example 3 in connection with Resin 13.
19. A process for producing a hydrocarbon resin, substantially as described in foregoing Example 4 in connection with Resin 14.
20. A process for producing a hydrocarbon resin, substantially as described in foregoing Example 4 in connection with Resin 15.
21. A process for producing a hydrocarbon resin, substantially as described in foregoing Example 4 in connection with Resin 16.
22. A process for producing a hydrocarbon resin, substantially as described in foregoing Example 5 in connection with Resin 17.
23. A process for producing a hydrocarbon resin, substantially as described in foregoing Example 5 in connection with Resin 18.
24. A process for producing a hydrocarbon resin, substantially as described in foregoing Example 5 in connection with Resin 19.

25. A process for producing a hydrocarbon resin, substantially as described in foregoing Example 6 in connection with Resin 20.

5 26. A process for producing a hydrocarbon resin, substantially as described in foregoing Example 6 in connection with Resin 21.

27. A process for producing a hydrocarbon resin, substantially as described in foregoing Example 6 in connection with Resin 22.

10 28. A hydrocarbon resin whenever produced by the process of any one of the preceding claims.

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